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(21)Application number : 10-326190 (71)Applicant : AGENCY OF IND SCIENCE &
TECHNOL

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SATO OSAMU

(54) METHOD FOR NONCATALYTIC SYNTHETIC ORGANIC REACTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for forming pinacoline by the pinacol rearrangement in supercritical water in which a remarkably high reaction velocity is obtained without adding a highly concentrated acid.

SOLUTION: A reaction velocity of an organic synthetic reaction is increased by using a proton feed from water in a noncatalytic condition without adding an acid catalyst in supercritical water. Pinacoline is produced in high reaction velocity by carrying out the pinacol rearrangement in a noncatalytic condition without adding an acid catalyst in supercritical water. A cyclic compound is formed from pinacol in the noncatalytic condition without adding an acid catalyst in the vicinity of the critical point (375-380° C, 22.5-25 Mpa) of supercritical water.

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CLAIMS

[Claim(s)]

[Claim 1] The non-catalyst organic synthesis approach characterized by performing an organic synthesis reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater using the proton supply from water.

[Claim 2] How to increase the reaction rate of an organic synthesis reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater using the proton supply from water.

[Claim 3] The pinacol rearrangement reaction approach characterized by generating pinacolin by performing a pinacol rearrangement reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater.

[Claim 4] The ring closure approach characterized by generating a ring compound from a pinacol under the non-catalyst which does not add an acid catalyst in near the critical point of supercritical water.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is a thing about the new supercritical water organic synthesis reaction approach which makes it possible to perform an organic synthesis reaction with a high reaction rate under the non-catalyst which does not add a high-concentration acid in supercritical underwater. The approach this invention increases the reaction rate of this organic synthesis reaction to the approach list which performs an organic synthesis reaction under a non-catalyst by supercritical underwater using the proton supply from water in more detail, And the ring closure approach which generates a ring compound from a pinacol under the non-catalyst which does not add an acid catalyst in near a supercritical point in the pinacol rearrangement reaction approach list which generates pinacolin by performing a pinacol rearrangement reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater, It is alike and is related.

[0002]

[Description of the Prior Art] Recently, in addition to the various advantages on a process, in the organic chemistry reaction which uses supercritical fluid as a reaction medium, a remarkable change of the reaction rate near the critical point of supercritical fluid or selectivity is reported (1-3; the number of the advanced-technology reference which carries out a postscript is shown.). Hereafter, it is the same. Attention is greatly attracted. Supercritical fluid has the middle physical property of a liquid and a gas, and its molecular motion energy is always more superior than intermolecular force. Those molecules were changed violently, still maintaining some order near the critical point, from dissipation by formation of the order of the system by intermolecular force and the kinetic energy of a molecule rivaling, if it sees micro (formation of a cluster). Therefore, near the critical point, fluid density changes with change of few temperature and pressures a lot.

[0003] In the organic synthesis reaction which uses such a supercritical liquid as a reaction medium, paying attention to a reaction molecule, it is found out that the chemical interaction between the different-species molecules in the minute field around it especially changes specifically near the critical point (4-5), and it is expected that change of dynamic [its] and static structure has big effect on the balance of a reaction, or a rate and product distribution.

[0004] Therefore, this invention persons are newly in, such as high-pressure FT-IR, UV/Vis, and Raman spectroscopy. A situ measuring method is developed and it is tackling solving the relation of the factor and micro reaction place which have affected the reactivity on a molecule scale. If these are realized, it does not come out of the relation between the function as a reaction place of supercritical fluid, and reactivity as much as possible clearly, it is considered that the micro reaction place formed into supercritical fluid is also controllable by macroscopic actuation, such as temperature and a pressure, and it may lead to the invention of a still newer alternative and high efficient chemical reaction process, and, also industrially, can expect.

[0005] While the application to the reaction place of such supercritical fluid is expected, the chemical reaction which makes supercritical water a reaction place with a supercritical carbon dioxide attracts attention in recent years. To the essence not changing fundamentally by non-

polar in the state of supercritical in a carbon dioxide, if water changes to a supercritical condition, having a completely different property from the water of ordinary temperature is known well. For example, near critical temperature, although the dielectric constant of the water under ordinary temperature and atmospheric pressure is about 80, since the dielectric constant of supercritical water is three to about 20, the dielectric constant of water is extensively [continuously and] controllable by temperature and the pressure. From this, the polar low organic substance like an aromatic compound and various gases may also be able to be dissolved in supercritical underwater, and the engineering value is very large.

[0006] Global attentions have gathered for the oxidative degradation (SCWO) of a toxic material which used the property of such supercritical water in this way (6). This is because an oxidizer like many harmful organic substance (for example, chlorinated aromatic compound), air, and oxygen dissolves in supercritical underwater easily and oxidative degradation (combustion) becomes possible. This invention persons have also succeeded in full decomposition of Polychlorinated biphenyl (PCB) by SCWO which used the hydrogen peroxide as the oxidizer (7). Furthermore, the possibility of the application is very large also as a reaction medium of thermal reaction, such as a synthetic reaction, a reduction reaction, a pyrolysis reaction, and dehydration, and the possibilities as a reaction solvent of supercritical water are specified.

[0007] Although the organic synthesis reaction in supercritical fluid attracts attention, there are very few examples of the organic synthesis reaction which the many are the chemical reactions which used the organic metal catalyst in the supercritical carbon dioxide, and made (8) and supercritical water the reaction place. It is thought from the property of the supercritical water that a nonpolar compound's being able to dissolve easily by supercritical underwater and its critical temperature are very high compared with it of a carbon dioxide that examination of a supercritical underwater organic synthesis reaction is very meaningful.

[0008] It became clear for hydrogen bond reinforcement to decrease remarkably (9, 10), and near the critical point of water by the latest research, and to have a dimer or monomer structure. Furthermore, according to research (11 12) of the supercritical water using this invention persons' Raman spectroscopy, or an elevated temperature and a high-pressure water solution, monomer structure was further decomposed by the structure instability near the critical point (change of dynamics), and it was suggested that possibility that a proton will generate is strong. If there are few places which can hold a proton in a system after proton generating, proton partial concentration should become high and should also affect chemical reactivity.

[0009] As mentioned above, various researches are advanced [reaction / in supercritical fluid (a carbon dioxide, water, ethane, propane, etc.) / organic chemistry] from a viewpoint of the physicochemical property of a solvent, a solvent, or the solute clustering effectiveness centering on near the critical point about the reaction rate, or the temperature and the pressure dependency of selectivity until now. Furthermore, many things are examined also about the possibility of the new chemical reaction invention including various chemical reactions in the inside of the supercritical fluid under catalyst existence, development of the spectroscopy-spot measuring method in the elevated temperature and a high-pressure reaction place like supercritical water, and an inorganic reaction. If the relation between the chemical reactivity in the inside of supercritical fluid and the micro factor of the field near the substrate molecule can be solved on a molecule scale, it leads to the function of the reaction place in a supercritical condition, a reactant elucidation, as a result the invention of an alternative and high efficient reaction process, and the usefulness can expect very much from the standpoint that it is [both] scientific and industrial. However, in the supercritical underwater organic synthesis reaction, most examples which attained the high reaction rate using the proton supply from water are not reported an old place.

[0010]

[Problem(s) to be Solved by the Invention] In such a situation, this invention persons check that a Beckmann rearrangement reaction advances with a non-catalyst in supercritical underwater. Furthermore, in situ observation of a non-catalyst pinacol rearrangement reaction is performed by supercritical underwater using the elevated-temperature high pressure FTIR. As a result of examining the possibility, the reaction rate of an organic synthesis reaction can be increased

under a non-catalyst by supercritical underwater using the proton supply from water. And that a very high rate constant is obtained by performing a pinacol rearrangement reaction by supercritical underwater and near the critical point (375 to 380 degree C, 22.5-25MPa) It shows clearly a header and that a ring compound generates from a pinacol further for a ring compound generating specifically in addition to pinacolin, and came to complete this invention. Namely, this invention aims at offering the approach of increasing the reaction rate of this organic synthesis reaction while it offers the approach of performing an organic synthesis reaction under a non-catalyst by supercritical underwater using the proton supply from water. Moreover, this invention aims at offering the approach of newly generating a ring compound from a pinacol near the critical point while it offers the pinacol rearrangement reaction approach which generates pinacolin by performing a pinacol rearrangement reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater.

[0011]

[Means for Solving the Problem] This invention for solving the above-mentioned technical problem consists of the following technical means.

- (1) The non-catalyst organic synthesis approach characterized by performing an organic synthesis reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater using the proton supply from water.
- (2) How to increase the reaction rate of an organic synthesis reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater using the proton supply from water.
- (3) The pinacol rearrangement reaction approach characterized by generating pinacolin by performing a pinacol rearrangement reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater.
- (4) The synthetic approach characterized by generating a ring compound from a pinacol under the non-catalyst which does not add an acid catalyst near the critical point of supercritical water (375 to 380 degree C, 22.5-25MPa).

[0012]

[Embodiment of the Invention] Next, this invention is further explained to a detail. In supercritical underwater, when this invention persons examined the possibility of a further supercritical underwater pinacol rearrangement reaction based on having checked that a Beckmann rearrangement reaction advanced with the non-catalyst, they found out that pinacolin generates under the non-catalyst which does not add an acid catalyst, and that the reaction rate of an organic synthesis reaction increased by proton supply from water. If the conventional pinacol rearrangement reaction does not add acids, such as a sulfuric acid and a hydrochloric acid, as a catalyst, perchloric acid and a hydrochloric acid are added by high concentration from there being no reaction advance, for example. Since a velocity constant also increases as acid concentration increases, it turns out that it is the reaction promoted by the proton which a reaction generates from an acid, i.e., an acid. Moreover, it also became clear that a ring compound generated from a pinacol.

[0013] this invention persons found out that the hydrogen bond structure broke remarkably near the critical point, while an elevated temperature and high-pressure Raman spectroscopy had been examining the structure of supercritical water (critical temperature of 375 degrees C, water of 22.05 or more MPas of critical pressure) for some time. However, the corroboration whether the hydrogen bond structure of water broke to a proton until now tried the pinacol rearrangement reaction next, in order that possibility that it will be referred to as that propose for the first time and the proton is supplied from supercritical water to perform the reaction in which a proton participates by supercritical underwater also in order to verify it since there was nothing might guess a large thing and might obtain the corroboration of proton supply from further more positive water.

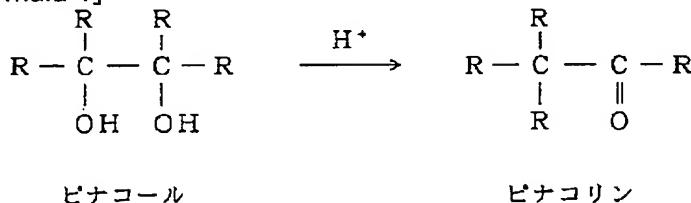
[0014] Consequently, this invention persons found out that the reaction rate of an organic synthesis reaction increases by proton supply from water by supercritical underwater, and that pinacolin generated with a high reaction rate by performing a pinacol rearrangement reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater. As the

example which carries out a postscript showed, it was completely unexpected by performing a supercritical underwater pinacol rearrangement reaction that a rate constant becomes very large. Moreover, when near the critical point was removed also about the product, things other than pinacolin used NMR and GC-MS other than IR, and checked not generating. Near the critical point of supercritical water, the dienes in which the dehydrator style of a pinacol has conjugated double bond unlike it of an above-mentioned pinacol rearrangement reaction generated, the Diels-Alder reaction occurred between the diene compounds generated further, and this invention persons found out that a ring compound newly generated. (13) which advances to a pinacol rearrangement reaction advancing under strong acid existence like a sulfuric acid and a hydrochloric acid under a weak acid existence [like a bromine chloride] whose dehydration from a pinacol to diene is -- by supercritical underwater, acid strength might change with temperature and pressures from things, and these results were completely unexpected things. About the product, it checked using GC-MS and NMR.

[0015] Since the above-mentioned rearrangement reaction is performed in the supercritical condition, although temperature is high (reacting at an elevated temperature a top difficult in equipment where a high-concentration acid is added) Even if possible, it will be thought that it is expected that the property of an acid changes a lot and that the meaning from which a very high reaction rate is obtained even if it does not add the high-concentration acid which brings bad effect to an environment in a rise of the consciousness to the latest environmental problem is very large. Furthermore, since a ring compound newly generates by different dehydrator style from a pinacol rearrangement reaction near the critical point of supercritical water, acid strength may be able to be changed only by temperature and the pressure and it is important also from a scientific and industrial standpoint supercritical underwater. Moreover, the above-mentioned rearrangement reaction is free water also with the cheap solvent to be used, and it can be said also from not using an organic solvent, either that it is the environment-friendly reacting method. By performing an organic synthesis reaction by this invention under the non-catalyst which does not add a supercritical underwater and high-concentration acid using the proton supply from water showed that a high reaction rate was obtained. Moreover, in the supercritical underwater pinacol rearrangement reaction, it turned out that a rate constant becomes very large. Furthermore, near the critical point of supercritical water, it turned out that a ring compound newly generates. Thus, effectiveness, such as the approach of increasing the reaction rate of an organic synthesis reaction to the approach list which performs an organic synthesis reaction using the proton supply from water under the non-catalyst which does not add an acid catalyst by the above-mentioned supercritical underwater It cannot be overemphasized that it will not prove without this invention persons, therefore the class will not be asked if this invention is not limited to one specific approach and these approaches are used, but it belongs to the approach of this invention.

[0016]

[Formula 1]



R : CH₃

[0017]

[Example] Next, although this invention is concretely explained based on an example, the following examples show the suitable example of this invention, and this invention is not limited at all by the following examples.

The schematic diagram of the circulation-type the elevated temperature and high-pressure

laser-Raman-spectroscopy system used by this example was shown in the schematic diagram 3 of an example 1 (1) system. First, after the measuring method carried out bubbling of high grade distilled water (3 times distillation) enough and deaerated it with nitrogen gas, it sent the filter continuously using through and the usual pump for high-speed liquid clos. The pressure was the precision of **0.1MPa by the back-pressure valve, and temperature produced the heating furnace of a mantle heater mold, and controlled it by the temperature controller. Proofreading of temperature measures a pressure at the temperature (for example, 350 degrees C) of the arbitration in a vapor-liquid coexistence two phase field, and is NBC/NRC. It carried out by comparing with the known temperature in the saturation point with reference to Table.

[0018] (2) The circulation type elevated temperature and the high-pressure FTIR system which experiment approach 1 elevated temperatures and high-pressure cel this invention persons built made possible a supercritical underwater successive reaction and in situ observation by IR. The schematic diagram of an elevated temperature and a high-pressure cel was shown in drawing 1. Use of the diamond as aperture material usually enabled measurement of an infrared region. Gold foil was inserted between a diamond aperture and shock absorbing material, it was used as a spacer, and the cel optical path length was adjusted. Although the optical path length was measured from the refractive index and interference fringe of water, and the pressure did not influence it, the optical path lengths increased in number with temperature, and became fixed above 400 degrees C 44.0 micrometers in 24.4 micrometers and 400 degrees C at 100 degrees C. Moreover, the volume (sum of the volume of piping in a path including the optical path in a cel and a heating furnace) of an active zone is 0.662ml.

[0019] 2) High grade distilled water fully deaerated by Approach helium was used for preparation of a pinacol [(CH₃)₂(OH)C(OH)(CH₃)₂] water solution, and the concentration was set to 0.422molal(s). Water or a pinacol water solution sent the liquid continuously with the liquid clo pump. The pressure was the precision of **0.1MPa by the back-pressure valve, and temperature produced the vacuum heating furnace of a mantle heater mold, and controlled it by the temperature controller in the precision of **0.2 degrees C. Temperature performed the reaction under the conditions room temperature -748K and whose pressure are 0.1 - 35MPa, and residence-time 120 - 8 seconds. After measurement of the IR spectrum of a reaction solution checked having sent the liquid by the fixed rate of flow, and having reached the balance, after reaching a predetermined pressure and temperature, it was measured by - with a resolution of 4cm⁻¹ and 50 counts of addition (1.2 second / scan).

[0020] (3) result 1 drawing 2 -- a pressure, each temperature, 0.1MPa, 20 degree-C(a)25MPa, 250 degree-C(b)25MPa, 38.5 degrees C (c), and residence time -- it was fixed for 108 seconds and the IR spectrum of 2000-800cm⁻¹ of the measured pinacol water solution was shown. The background spectrum of the pure water which measured all on these conditions amended. The biggest change all over drawing is the point that the absorption peak of 945cm⁻¹ of (a) and (b) disappeared in (c), and absorption strong against 1700cm⁻¹ newly appeared. It turns out that the new matter generated specifically under the conditions of (c) clearly. Since 945cm⁻¹ was the number of OH deformation vibration of alcohol, and the C=O stretching frequency of an aliphatic series ketone with typical 1700cm⁻¹, the rearrangement reaction of a pinacol arose, and it was thought that pinacolin [(CH₃)₃CCOCH₃] had generated. Furthermore, GC-MS and NMR analyzed and the generation was checked. While beginning to promote a pinacol rearrangement reaction with a non-catalyst in supercritical underwater from the above result and finding out, the proton generation from supercritical water itself was checked.

[0021] (4) The rate constant obtained by the result 2, next experiment conditions and this invention is shown. In addition, the rate constant was processed as primary rate constant like other reference, and using circulation-type the elevated temperature and high-pressure FTIR equipment which this invention persons developed, the measuring method changed the temperature of a pinacolin water solution, a pressure, and residence time, and was calculated from the percentage reduction of the characteristic absorption wave number (OH deformation vibration) of pinacolin. In addition, at temperature lower than the temperature of 250 degrees C, pinacolin generated with neither of the pressures.

1) experiment condition PINARU water-solution concentration 0.4M temperature 20 degree-C-

450 degree-C pressure 0.1, 20, 22.05, 25 and 30, and 35MPa residence time 50 -- the class of pinacol used in addition m seconds to 120 a second -- R=CH3 it is .

[0022] 2) Result (pressure 25MPa)

Temperature (degree C) Rate constant (S-1) ..

300 1.26x10-1350 2.37x10-1370 3.41x10-1385 3.58x10-1395 5.41x10-1400 5.66x10-1425

1.32450 1.96 (pressure 30MPa)

Temperature (degree C) Rate constant (S-1)

300 1.26X10-1350 3.38X10-1370 4.52X10-1385 4.55X10-1395 7.36X10-1410 8.07X10-1430 1.73

(Pressure 35MPa)

Temperature (degree C) Rate constant (S-1)

300 3.56X10-1370 3.43X10-1385 3.58X10-1395 4.52X10-1425 0.87X10-1450 1.45 [0023]

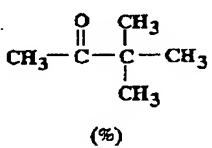
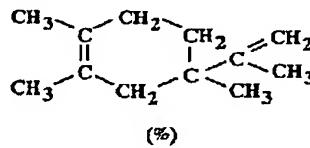
Although it changed also with the acid concentration of the result to compare, and temperature, even if compared with the conventional approach (HClO40.71M, temperature of 113.5 degrees C), the increment in one about 600 times the rate constant of this was acquired. moreover -- although this reaction is performed under high pressure like this invention using the 0.871M hydrochloric-acid catalyst by the conventional reference (The Review of Physical Chemistry of Japan, Vol.40, No.1, and 1970), if 46.7MPa(s) of this invention persons' best research result and the above-mentioned conventional reference and the case of 70 degrees C are compared -- 1.5x105 It turns out that it also increases twice.

[0024] (5) The product compounded from the pinacol [(CH3)2(OH)C(OH)(CH3)2] under the supercritical underwater non-catalyst and its selectivity are shown in a result 3, next Table 1. Generation of the pinacolin [(CH3)2COCH3] shown in Table 1 as a product and a 1, 2, and 5-trimethyl-5-isopropenyl-1-cyclohexene was checked by GC-MS and NMR. About selectivity, although the 1, 2, and 5-trimethyl-5-isopropenyl-1-cyclohexene was like about 20%, only in near the critical point, it generated specifically. Moreover, under the other conditions, pinacolin generated at 100% of a rate. In addition, experiment conditions are the same as the case of a result 2.

[0025]

[Table 1]

表1 生成物分布

条件	 (%)	 (%)
375~380°C 22.05~25MPa	77%	23%
上記条件以外 の超臨界水中	100%	0%

[0026] as past research, globally an above supercritical underwater synthetic reaction does not almost have an example of a report, and a supercritical underwater Diels-Alder reaction comes out of it to some extent except research of this invention persons. Incidentally, there are many examples of a report about a supercritical underwater decomposition reaction.

[0027]

[Effect of the Invention] The approach this invention increases the reaction rate of an organic synthesis reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater using the proton supply from water as explained in full detail above, It is a thing concerning the approach of generating a ring compound from a pinacol in the approach and near the critical point etc. by this invention [which generate pinacolin by performing a pinacol rearrangement reaction] (1) Pinacolin is generable under the non-catalyst which does not add

an acid catalyst. (2) A rate constant can be extremely enlarged by performing a supercritical underwater pinacol rearrangement reaction. (3) Even if it does not add a high-concentration acid, a very high reaction rate is obtained. (4) near the critical point of (5) supercritical water with which a pinacol rearrangement reaction is promoted under the non-catalyst which does not add an acid catalyst by supercritical underwater A ring compound is newly compoundable using change of the acid strength of supercritical water. (6) The effectiveness according to rank of ** that the environment-friendly synthetic reacting method for the ability to perform the organic synthesis reaction using the proton supplied from supercritical water which does not use the acid or organic solvent of (7) high concentration can be offered is done so.

[0028] Below, advanced-technology reference is shown.

1 J. B. Ellington, J. F. Brennecke, J. Chem., Soc. Chem. Commun., 1094(1993)2 Y. Ikushima, No. Saito, T. Yokoyama, K. Hatakeda, S. Ito, M. Arai, H. W. Blanch, Chem. Lett, 108 (1993)3 P. G. Jessop, T. Ikariya, R. Noyori, Science, 269, 1065 (1995)4 Y. P.Sun, M.A.Fox, and K. P.Johnston and J.Am. Chem.Soc., 114, and 1187 (1992) 5 A.A.Chialvo, P.G.Debenedetti and Ind. Eng.Chem.Res. and 31, 1391 6 (1992) E.T.Ryan, T.Xiang and K.P.Johnston, M.A.Fox and J.Phys. Chem. and 1009365 7 (1996) K.Hatakeda and Y.Ikushima, S.Ito, O.Sato, and N. Saito and Chem.Lett., 245 8 (1997) M.J.Burk, S.Feng and M.F.Gross, W.Tumas and J.Am.Chem. Soc., 117, and 8277 9 (1995) N.Matsubayashi and C. Wakui and M.Nakahara, Phys.Rev.Lett. and 78, 2573 10 (1997) M.M. Hoffmann and S.Conradi, J.Am.Chem.Soc. and 119, 3811 11 (1997) Y.Ikushima, K.Hatakeda, N.Saito, and M. Arai and J.Chem.Phys., 108 5855 12 (1998) Y. Ikushima and N.Saito, M.Arai, J.Phys.Chem.B, 102, 3029 13 (1998) C.F.R.Allen, A.Bell, Org.Syntheses Coll., 3, and 312 (1955)

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the new supercritical water organic synthesis reaction approach which makes it possible to perform an organic synthesis reaction with a high reaction rate under the non-catalyst which does not add a high-concentration acid in supercritical underwater. The approach this invention increases the reaction rate of this organic synthesis reaction to the approach list which performs an organic synthesis reaction under a non-catalyst by supercritical underwater using the proton supply from water in more detail, And the ring closure approach which generates a ring compound from a pinacol under the non-catalyst which does not add an acid catalyst in near a supercritical point in the pinacol rearrangement reaction approach list which generates pinacolin by performing a pinacol rearrangement reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater, It is alike and is related.

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[0005] While the application to the reaction place of such supercritical fluid is expected, the chemical reaction which makes supercritical water a reaction place with a supercritical carbon dioxide attracts attention in recent years. To the essence not changing fundamentally by non-polar in the state of supercritical in a carbon dioxide, if water changes to a supercritical condition, having a completely different property from the water of ordinary temperature is known well. For example, near critical temperature, although the dielectric constant of the water under ordinary temperature and atmospheric pressure is about 80, since the dielectric constant of supercritical water is three to about 20, the dielectric constant of water is extensively [continuously and] controllable by temperature and the pressure. From this, the polar low organic substance like an aromatic compound and various gases may also be able to be dissolved in supercritical underwater, and the engineering value is very large.

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Furthermore, the possibility of the application is very large also as a reaction medium of thermal reaction, such as a synthetic reaction, a reduction reaction, a pyrolysis reaction, and dehydration, and the possibilities as a reaction solvent of supercritical water are specified.

[0007] Although the organic synthesis reaction in supercritical fluid attracts attention, there are very few examples of the organic synthesis reaction which the many are the chemical reactions which used the organic metal catalyst in the supercritical carbon dioxide, and made (8) and supercritical water the reaction place. It is thought from the property of the supercritical water that a nonpolar compound's being able to dissolve easily by supercritical underwater and its critical temperature are very high compared with it of a carbon dioxide that examination of a supercritical underwater organic synthesis reaction is very meaningful.

[0008] It became clear for hydrogen bond reinforcement to decrease remarkably (9, 10), and near the critical point of water by the latest research, and to have a dimer or monomer structure. Furthermore, according to research (11 12) of the supercritical water using this invention persons' Raman spectroscopy, or an elevated temperature and a high-pressure water solution, monomer structure was further decomposed by the structure instability near the critical point (change of dynamics), and it was suggested that possibility that a proton will generate is strong. If there are few places which can hold a proton in a system after proton generating, proton partial concentration should become high and should also affect chemical reactivity.

[0009] As mentioned above, various researches are advanced [reaction / in supercritical fluid (a carbon dioxide, water, ethane, propane, etc.) / organic chemistry] from a viewpoint of the physicochemical property of a solvent, a solvent, or the solute clustering effectiveness centering on near the critical point about the reaction rate, or the temperature and the pressure dependency of selectivity until now. Furthermore, many things are examined also about the possibility of the new chemical reaction invention including various chemical reactions in the inside of the supercritical fluid under catalyst existence, development of the spectroscopy-spot measuring method in the elevated temperature and a high-pressure reaction place like supercritical water, and an inorganic reaction. If the relation between the chemical reactivity in the inside of supercritical fluid and the micro factor of the field near the substrate molecule can be solved on a molecule scale, it leads to the function of the reaction place in a supercritical condition, a reactant elucidation, as a result the invention of an alternative and high efficient reaction process, and the usefulness can expect very much from the standpoint that it is [both] scientific and industrial. However, in the supercritical underwater organic synthesis reaction, most examples which attained the high reaction rate using the proton supply from water are not reported an old place.

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EFFECT OF THE INVENTION

[Effect of the Invention] This invention relates to the approach of generating a ring compound from a pinacol in the approach of increasing the reaction rate of an organic synthesis reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater using the proton supply from water, the approach of generating pinacolin by performing a pinacol rearrangement reaction, and near the critical point etc. as explained in full detail above. Pinacolin is generable with this invention under the non-catalyst which does not add (1) acid catalyst. (2) A rate constant can be extremely enlarged by performing a supercritical underwater pinacol rearrangement reaction. (3) Even if it does not add a high-concentration acid, a very high reaction rate is obtained. (4) near the critical point of (5) supercritical water with which a pinacol rearrangement reaction is promoted under the non-catalyst which does not add an acid catalyst by supercritical underwater A ring compound is newly compoundable using change of the acid strength of supercritical water. (6) The effectiveness according to rank of ** that the environment-friendly synthetic reacting method for the ability to perform the organic synthesis reaction using the proton supplied from supercritical water which does not use the acid or organic solvent of (7) high concentration can be offered is done so.

[0028] Below, advanced-technology reference is shown.

1 J. B. Ellington, J. F. Brennecke, J. Chem., Soc. Chem. Commun., 1094(1993)2 Y. Ikushima, No. Saito, T. Yokoyama, K. Hatakeyama, S. Ito, M. Arai, H. W. Blanch, Chem. Lett, 108 (1993)3 P. G. Jessop, T. Ikariya, R. Noyori, Science, 269, 1065 (1995)4 Y. P. Sun, M. A. Fox and K. P. Johnston and J. Am. Chem. Soc., 114, and 1187 (1992) 5 A.A. Chialvo, P.G. Debenedetti and Ind. Eng. Chem. Res. and 31, 1391 6 (1992) E.T. Ryan, T. Xiang and K.P. Johnston, M.A. Fox and J. Phys. Chem. and 1009365-7 (1996) K. Hatakeyama and Y. Ikushima, S. Ito, O. Sato, and N. Saito and Chem. Lett., 245 8 (1997) M.J. Burk, S. Feng and M.F. Gross, W. Tumas and J. Am. Chem. Soc., 117, and 8277 9 (1995) N. Matsubayashi and C. Wakui and M. Nakahara, Phys. Rev. Lett. and 78, 2573 10 (1997) M.M. Hoffmann and S. Conradi, J. Am. Chem. Soc. and 119, 3811 11 (1997) Y. Ikushima, K. Hatakeyama, N. Saito, and M. Arai and J. Chem. Phys., 108 5855 12 (1998) Y. Ikushima and N. Saito, M. Arai, J. Phys. Chem. B, 102, 3029 13 (1998) C.F.R. Allen, A. Bell, Org. Syntheses Coll., 3, 312
 (1955)

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] In such a situation, this invention persons check that a Beckmann rearrangement reaction advances with a non-catalyst in supercritical underwater. Furthermore, in situ observation of a non-catalyst pinacol rearrangement reaction is performed by supercritical underwater using the elevated-temperature high pressure FTIR. As a result of examining the possibility, the reaction rate of an organic synthesis reaction can be increased under a non-catalyst by supercritical underwater using the proton supply from water. And that a very high rate constant is obtained by performing a pinacol rearrangement reaction by supercritical underwater and near the critical point (375 to 380 degree C, 22.5-25MPa) It shows clearly a header and that a ring compound generates from a pinacol further for a ring compound generating specifically in addition to pinacolin, and came to complete this invention. Namely, this invention aims at offering the approach of increasing the reaction rate of this organic synthesis reaction while it offers the approach of performing an organic synthesis reaction under a non-catalyst by supercritical underwater using the proton supply from water. Moreover, this invention aims at offering the approach of newly generating a ring compound from a pinacol near the critical point while it offers the pinacol rearrangement reaction approach which generates pinacolin by performing a pinacol rearrangement reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater.

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MEANS

[Means for Solving the Problem] This invention for solving the above-mentioned technical problem consists of the following technical means.

- (1) The non-catalyst organic synthesis approach characterized by performing an organic synthesis reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater using the proton supply from water.
- (2) How to increase the reaction rate of an organic synthesis reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater using the proton supply from water.
- (3) The pinacol rearrangement reaction approach characterized by generating pinacolin by performing a pinacol rearrangement reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater.
- (4) The synthetic approach characterized by generating a ring compound from a pinacol under the non-catalyst which does not add an acid catalyst near the critical point of supercritical water (375 to 380 degree C, 22.5-25MPa).

[0012]

[Embodiment of the Invention] Next, this invention is further explained to a detail. In supercritical underwater, when this invention persons examined the possibility of a further supercritical underwater pinacol rearrangement reaction based on having checked that a Beckmann rearrangement reaction advanced with the non-catalyst, they found out that pinacolin generates under the non-catalyst which does not add an acid catalyst, and that the reaction rate of an organic synthesis reaction increased by proton supply from water. If the conventional pinacol rearrangement reaction does not add acids, such as a sulfuric acid and a hydrochloric acid, as a catalyst, perchloric acid and a hydrochloric acid are added by high concentration from there being no reaction advance, for example. Since a velocity constant also increases as acid concentration increases, it turns out that it is the reaction promoted by the proton which a reaction generates from an acid, i.e., an acid. Moreover, it also became clear that a ring compound generated from a pinacol.

[0013] this invention persons found out that the hydrogen bond structure broke remarkably near the critical point, while an elevated temperature and high-pressure Raman spectroscopy had been examining the structure of supercritical water (critical temperature of 375 degrees C, water of 22.05 or more MPas of critical pressure) for some time. However, the corroboration whether the hydrogen bond structure of water broke to a proton until now tried the pinacol rearrangement reaction next, in order that possibility that it will be referred to as that propose for the first time and the proton is supplied from supercritical water to perform the reaction in which a proton participates by supercritical underwater also in order to verify it since there was nothing might guess a large thing and might obtain the corroboration of proton supply from further more positive water.

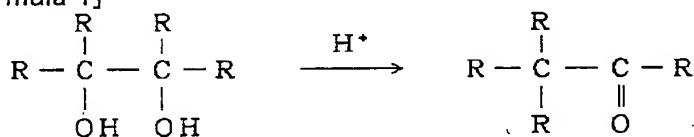
[0014] Consequently, this invention persons found out that the reaction rate of an organic synthesis reaction increases by proton supply from water by supercritical underwater, and that pinacolin generated with a high reaction rate by performing a pinacol rearrangement reaction under the non-catalyst which does not add an acid catalyst by supercritical underwater. As the

example which carries out a postscript showed, it was completely unexpected by performing a supercritical underwater pinacol rearrangement reaction that a rate constant becomes very large. Moreover, when near the critical point was removed also about the product, things other than pinacolin used NMR and GC-MS other than IR, and checked not generating. Near the critical point of supercritical water, the dienes in which the dehydrator style of a pinacol has conjugated double bond unlike it of an above-mentioned pinacol rearrangement reaction generated, the Diels-Alder reaction occurred between the diene compounds generated further, and this invention persons found out that a ring compound newly generated. (13) which advances to a pinacol rearrangement reaction advancing under strong acid existence like a sulfuric acid and a hydrochloric acid under a weak acid existence [like a bromine chloride] whose dehydration from a pinacol to diene is -- by supercritical underwater, acid strength might change with temperature and pressures from things, and these results were completely unexpected things. About the product, it checked using GC-MS and NMR.

[0015] Since the above-mentioned rearrangement reaction is performed in the supercritical condition, although temperature is high (reacting at an elevated temperature a top difficult in equipment where a high-concentration acid is added) Even if possible, it will be thought that it is expected that the property of an acid changes a lot and that the meaning from which a very high reaction rate is obtained even if it does not add the high-concentration acid which brings bad effect to an environment in a rise of the consciousness to the latest environmental problem is very large. Furthermore, since a ring compound newly generates by different dehydrator style from a pinacol rearrangement reaction near the critical point of supercritical water, acid strength may be able to be changed only by temperature and the pressure and it is important also from a scientific and industrial standpoint supercritical underwater. Moreover, the above-mentioned rearrangement reaction is free water also with the cheap solvent to be used, and it can be said also from not using an organic solvent, either that it is the environment-friendly reacting method. By performing an organic synthesis reaction by this invention under the non-catalyst which does not add a supercritical underwater and high-concentration acid using the proton supply from water showed that a high reaction rate was obtained. Moreover, in the supercritical underwater pinacol rearrangement reaction, it turned out that a rate constant becomes very large. Furthermore, near the critical point of supercritical water, it turned out that a ring compound newly generates. Thus, effectiveness, such as the approach of increasing the reaction rate of an organic synthesis reaction to the approach list which performs an organic synthesis reaction using the proton supply from water under the non-catalyst which does not add an acid catalyst by the above-mentioned supercritical underwater It cannot be overemphasized that it will not prove without this invention persons, therefore the class will not be asked if this invention is not limited to one specific approach and these approaches are used, but it belongs to the approach of this invention.

[0016]

[Formula 1]



ビナコール

ビナコリン

R : CH₃

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EXAMPLE

[Example] Next, although this invention is concretely explained based on an example, the following examples show the suitable example of this invention, and this invention is not limited at all by the following examples.

The schematic diagram of the circulation-type the elevated temperature and high-pressure laser-Raman-spectroscopy system used by this example was shown in the schematic diagram 3 of an example 1 (1) system. First, after the measuring method carried out bubbling of high grade distilled water (3 times distillation) enough and deaerated it with nitrogen gas, it sent the filter continuously using through and the usual pump for high-speed liquid clos. The pressure was the precision of **0.1MPa by the back-pressure valve, and temperature produced the heating furnace of a mantle heater mold, and controlled it by the temperature controller. Proofreading of temperature measures a pressure at the temperature (for example, 350 degrees C) of the arbitration in a vapor-liquid coexistence two phase field, and is NBC/NRC. It carried out by comparing with the known temperature in the saturation point with reference to Table.

[0018] (2) The circulation type elevated temperature and the high-pressure FTIR system which experiment approach 1 elevated temperatures and high-pressure cel this invention persons built made possible a supercritical underwater successive reaction and in situ observation by IR. The schematic diagram of an elevated temperature and a high-pressure cel was shown in drawing 1. Use of the diamond as aperture material usually enabled measurement of an infrared region. Gold foil was inserted between a diamond aperture and shock absorbing material, it was used as a spacer, and the cel optical path length was adjusted. Although the optical path length was measured from the refractive index and interference fringe of water, and the pressure did not influence it, the optical path lengths increased in number with temperature, and became fixed above 400 degrees C 44.0 micrometers in 24.4 micrometers and 400 degrees C at 100 degrees C. Moreover, the volume (sum of the volume of piping in a path including the optical path in a cel and a heating furnace) of an active zone is 0.662ml.

[0019] 2) High grade distilled water fully deaerated by Approach helium was used for preparation of a pinacol [(CH₃)₂(OH)C(OH)(CH₃)₂] water solution, and the concentration was set to 0.422molal(s). Water or a pinacol water solution sent the liquid continuously with the liquid clo pump. The pressure was the precision of **0.1MPa by the back-pressure valve, and temperature produced the vacuum heating furnace of a mantle heater mold, and controlled it by the temperature controller in the precision of **0.2 degrees C. Temperature performed the reaction under the conditions room temperature -748K and whose pressure are 0.1 - 35MPa, and residence-time 120 - 8 seconds. After measurement of the IR spectrum of a reaction solution checked having sent the liquid by the fixed rate of flow, and having reached the balance, after reaching a predetermined pressure and temperature, it was measured by - with a resolution of 4cm⁻¹ and 50 counts of addition (1.2 second / scan).

[0020] (3) result 1 drawing 2 -- a pressure, each temperature, 0.1MPa, 20 degree-C(a)25MPa, 250 degree-C(b)25MPa, 38.5 degrees C (c), and residence time -- it was fixed for 108 seconds and the IR spectrum of 2000-800cm⁻¹ of the measured pinacol water solution was shown. The background spectrum of the pure water which measured all on these conditions amended. The biggest change all over drawing is the point that the absorption peak of 945cm⁻¹ of (a) and (b)

disappeared in (c), and absorption strong against 1700cm⁻¹ newly appeared. It turns out that the new matter generated specifically under the conditions of (c) clearly. Since 945cm⁻¹ was the number of OH deformation vibration of alcohol, and the C=O stretching frequency of an aliphatic series ketone with typical 1700cm⁻¹, the rearrangement reaction of a pinacol arose, and it was thought that pinacolin [(CH₃)₃COCH₃] had generated. Furthermore, GC-MS and NMR analyzed and the generation was checked. While beginning to promote a pinacol rearrangement reaction with a non-catalyst in supercritical underwater from the above result and finding out, the proton generation from supercritical water itself was checked.

[0021] (4) The rate constant obtained by the result 2, next experiment conditions and this invention is shown. In addition, the rate constant was processed as primary rate constant like other reference, and using circulation-type the elevated temperature and high-pressure FTIR equipment which this invention persons developed, the measuring method changed the temperature of a pinacolin water solution, a pressure, and residence time, and was calculated from the percentage reduction of the characteristic absorption wave number (OH deformation vibration) of pinacolin. In addition, at temperature lower than the temperature of 250 degrees C, pinacolin generated with neither of the pressures.

1) experiment condition PINARU water-solution concentration 0.4M temperature 20 degree-C-450 degree-C pressure 0.1, 20, 22.05, 25 and 30, and 35MPa residence time 50 -- the class of pinacol used in addition m seconds to 120 a second -- R=CH₃ it is .

[0022] 2) Result (pressure 25MPa)

Temperature (degree C) Rate constant (S-1)

300 1.26x10-1350 2.37x10-1370 3.41x10-1385 3.58x10-1395 5.41x10-1400 5.66x10-1425

1.32450 1.96 (pressure 30MPa)

Temperature (degree C) Rate constant (S-1)

300 1.26X10-1350 3.38X10-1370 4.52X10-1385 4.55X10-1395 7.36X10-1410 8.07X10-1430 1.73

(Pressure 35MPa)

Temperature (degree C) Rate constant (S-1)

300 3.56X10-1370 3.43X10-1385 3.58X10-1395 4.52X10-1425 0.87X10-1450 1.45 [0023]

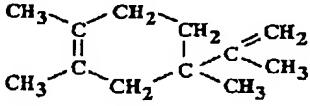
Although it changed also with the acid concentration of the result to compare, and temperature, even if compared with the conventional approach (HClO40.71M, temperature of 113.5 degrees C), the increment in one about 600 times the rate constant of this was acquired. moreover -- although this reaction is performed under high pressure like this invention using the 0.871M hydrochloric-acid catalyst by the conventional reference (The Review of Physical Chemistry of Japan, Vol.40, No.1, and 1970), if 46.7MPa(s) of this invention persons' best research result and the above-mentioned conventional reference and the case of 70 degrees C are compared -- 1.5x10⁵ It turns out that it also increases twice.

[0024] (5) The product compounded from the pinacol [(CH₃)₂(OH)C(OH)(CH₃)₂] under the supercritical underwater non-catalyst and its selectivity are shown in a result 3, next Table 1. Generation of the pinacolin [(CH₃)₃COCH₃] shown in Table 1 as a product and a 1, 2, and 5-trimethyl-5-isopropenyl-1-cyclohexene was checked by GC-MS and NMR. About selectivity, although the 1, 2, and 5-trimethyl-5-isopropenyl-1-cyclohexene was like about 20%, only in near the critical point, it generated specifically. Moreover, under the other conditions, pinacolin generated at 100% of a rate. In addition, experiment conditions are the same as the case of a result 2.

[0025]

[Table 1]

表1 生成物分布

条件	$\text{CH}_3-\text{C}(=\text{O})-\text{C}(\text{CH}_3)-\text{CH}_3$ (%)	 (%)
375~380°C 22.05~25 MPa	77%	23%
上記条件以外 の超臨界水中	100%	0%

[0026] as past research, globally an above supercritical underwater synthetic reaction does not almost have an example of a report, and a supercritical underwater Diels-Alder reaction comes out of it to some extent except research of this invention persons. Incidentally, there are many examples of a report about a supercritical underwater decomposition reaction.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram of an elevated temperature and a high-pressure cel.

[Drawing 2] It is the IR spectrum of 2000-800cm⁻¹ of a pinacol water solution.

[Drawing 3] It is the schematic diagram of a circulation-type an elevated temperature and a quantity laser-Raman-spectroscopy system.

[Description of Notations]

- 1) Body (Hastelloy C-276)
- 2) The body which fixes a diamond aperture
- 3) Molybdenum which puts a diamond aperture
- 4) Diamond aperture

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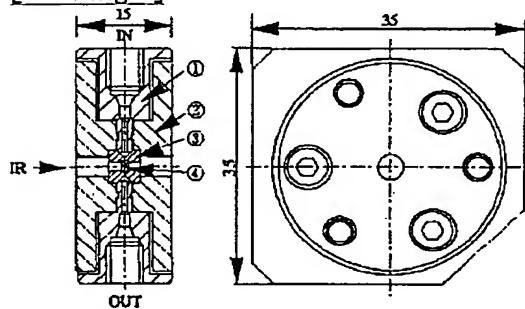
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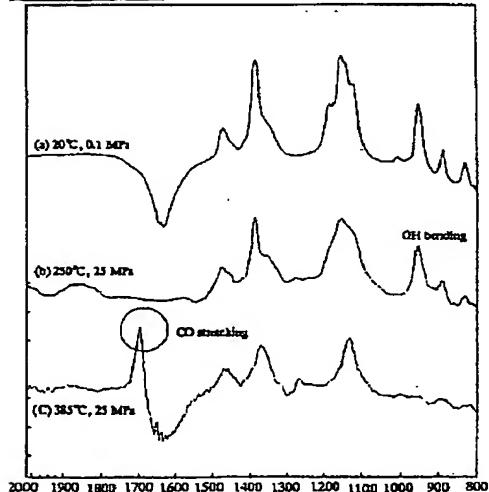
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DRAWINGS

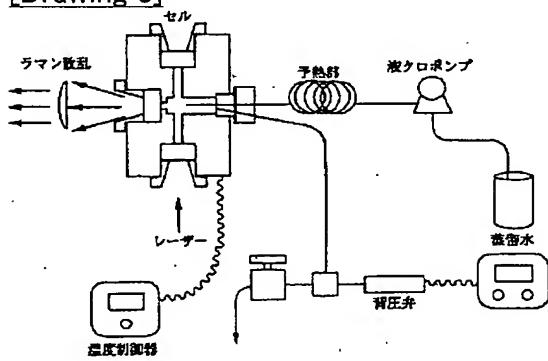
[Drawing 1]

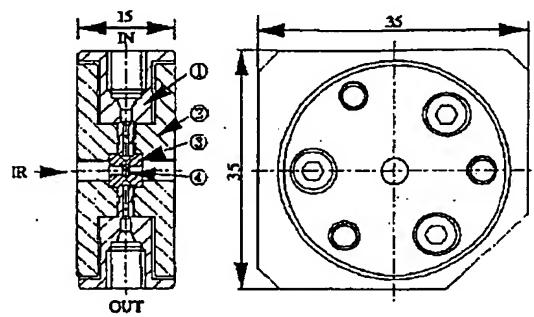


[Drawing 2]



[Drawing 3]



Drawing selection drawing 1 

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